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Transition metal chemistry of phosphorus based ligands. Ruthenium(II) chemistry of bis(phosphino)amines, $X_2PN(R)PX_2$ ($R = H$ or Ph, $X = Ph$; $R = Ph$, $X_2 = O_2C_6H_4$)

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Abstract

Reactions of $CpRuCl(PPh_3)_2$ with bis(phosphino)amines, $X_2PN(R)PX_2$ (**1** $R = H$, $X = Ph$; **2** $R = X = Ph$; **3** $R = Ph$, $X_2 = O_2C_6H_4$) give neutral or cationic mononuclear complexes depending on the reaction conditions. Reaction of **1** with $CpRuCl(PPh_3)_2$ gives one neutral complex, $[CpRu(Cl)(\eta^2\text{-}Ph_2PN(H)PPh_2)]$ (**4**) and two cationic complexes, $[CpRu(\eta^2\text{-}Ph_2PN(H)PPh_2)(\eta^1\text{-}Ph_2PN(H)PPh_2)]Cl$ (**5**) and $[CpRu(PPh_3)(\eta^2\text{-}Ph_2PN(H)PPh_2)]Cl$ (**6**), whereas the reaction of **2** with $CpRuCl(PPh_3)_2$ leads only to the isolation of cationic complex, $[CpRu(PPh_3)(\eta^2\text{-}Ph_2PN(Ph)PPh_2)]Cl$ (**7**). The catechol derivative **3**, in a similar reaction, affords an interesting mononuclear complex $[CpRu(PPh_3)\{\eta^1\text{-}(C_6H_4O_2)PN(Ph)P(O_2H_4C_6)\}_2]Cl$ (**8**) containing two monodentate bis(phosphino)amine ligands. The structural elucidation of the complexes was carried out by elemental analyses, IR and NMR spectroscopic data. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bis(phosphino)amines; Mononuclear; Ruthenium(II) complexes; Cationic; Monodentate; Bidentate

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1. Introduction

The synthesis and structural chemistry of ruthenium complexes containing *tertiary* mono- and bis(phosphine)s have attracted considerable interest in recent years [1–8]. Besides their potential use in classical catalytic processes such as hydrogenation, isomerization, decarbonylation, etc. [9–13], processes such as reductive elimination and oxidative addition for making and breaking C–H bonds [14–21], formation and cleavage of N–H and O–H bonds [22] were also observed in monomeric complexes that are stabilized by one or more *tertiary* mono- or bis(phosphine)s. The thermal and mechanistic aspects [23] along with the synthesis of new bis(phosphine) complexes are also interesting in view of their assistance in understanding the catalytic processes that take place at metal sites. By choosing an appropriate ligand system it is possible to fine tune the electronic and steric properties of the donor centers to bind the metals in desired oxidation state with a specific coordination number so that a catalyst may be generated for a specific organic transformation. In this context bis(phosphino)amines play a major role because of easy and high yield synthetic methodologies and flexibility in their reactivity toward transition metals in their various oxidation states [24–26]. As a part of our interest in this area [26–32], the above considerations prompted us to study the chemistry of bis(phosphino)amines, $X_2PN(R)PX_2$ (**1** $R = H$, $X = Ph$; **2** $R = X = Ph$; **3** $R = Ph$, $X_2 = O_2C_6H_4$) with the versatile ruthenium(II) complex such as $CpRuCl(PPh_3)_2$. Of concern in the present study was to show the versatility of the bis(phosphino)amine ligands in exhibiting different coordination behavior when the donor–acceptor properties are altered by incorporating different substituents at both the phosphorus centers and at the bridging nitrogen atom.

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2. Experimental section

All experimental manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried and distilled prior to use. $Ph_2PN(Ph)PPh_2$ [33], $Ph_2PN(H)PPh_2$ [34], $(C_6H_4O_2)PN(Ph)P(O_2H_4C_6)$ [32] and $CpRuCl(PPh_3)_2$ [35] were prepared according to published procedures or with minor modifications thereof. ^1H- and ^{31}P-NMR spectra were recorded on a VXR 300S spectrometer operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. $CDCl_3$ was used as both solvent and internal lock. Positive shifts lie downfield in all cases. IR spectra were recorded on FTIR Nicolet Impact 400 spectrometer in nujol mull or KBr disk. Microanalyses were carried out in the Department of Chemistry, IIT, Powai.

*2.1. Preparation of [CpRu(Cl)(η^2-$Ph_2PN(H)PPh_2$)] (**4**)*

A solution of $Ph_2PN(H)PPh_2$ (0.026 g, 0.068 mmol) in toluene (8 ml) was added dropwise to a solution of $CpRuCl(PPh_3)_2$ (0.050 g, 0.068 mmol), also in toluene (8 ml) and the reaction mixture was stirred at 80°C for 6 h. A clear solution was obtained. The solution was cooled to room temperature (r.t.) and 3 ml of *n*-hexane was added. An orange-colored crystalline product was precipitated which was isolated by filtration and then dried under vacuum.

Orange/red crystals, yield 78% (0.031 g), m.p. 179–181°C. Anal. Found: C 61.48, H 4.81, N 2.10%. Calc. for $C_{29}H_{26}NP_2Cl \cdot 0.5C_6H_5CH_3$ [36]: C 61.49, H 4.73, N 2.21%. IR (KBr) [37] ν_{max}: 3115m, 3054m, 2934sh, 2853s, 1238m, 1103sh, 1030s, 802sh, 695sh cm^{-1}. ^1H-NMR ($CDCl_3$) [38]: δ Phenyl region, 7.44 (m, 20H), δ Cp, 4.42 (s, 5H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 72.6 (s).

2.2. Reaction of $Ph_2PN(H)PPh_2$ with $CpRuCl(PPh_3)_2$ in 2:1 molar ratio

A solution of $Ph_2PN(H)PPh_2$ (0.054 g, 0.14 mmol) in toluene (8 ml) was added dropwise to a solution of $CpRuCl(PPh_3)_2$ (0.050 g, 0.068 mmol) also in toluene(8 ml) and the reaction mixture was heated to 80°C for 8 h. A clear solution was obtained at the end of the reaction to which 3 ml of *n*-hexane was added. An orange-colored crystalline product obtained was found to be a mixture of three products **4**, **5** and **6** identified by ^{31}P-NMR spectrum. The relative yields calculated from ^{31}P-NMR spectrum for **4**, **5** and **6** were 20, 65 and 15%, respectively.

When the reaction was carried out using two equivalents of ligand **1** with one equivalent of $CpRuCl(PPh_3)_2$ the yields of **5** and **6** were 90 and 10%, respectively, and there was no evidence for the formation of **4**, evidence by ^{31}P-NMR spectroscopy. The analytically-pure product **5** was obtained by crystallizing in a 1:3 mixture of dichloromethane and *n*-hexane.

Complex **5**: Orange crystalline material, m.p. 167°C (decomposes). Anal. Found: C 65.28, H 4.78, N 2.67%. Calc. for $C_{53}H_{47}N_2P_4RuCl$: C 65.46, H 4.83, N 2.88%. IR (nujol) ν_{max}:3312 m, 3065 s, 2930s, 1600vs, 1235 vs, 1110m, 1015m, 975m, 810sh, 795 m, 680 m cm^{-1}. ^1H-NMR ($CDCl_3$): δ phenyl, 7.26 (m, 40H), δ Cp, 4.40 (s, 5H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ (P_r) 60.6 (d), δ (P_c) 92.1 (td), δ (P_u) 31.2(d), $J_{PrPc} = 40.4$ Hz, $J_{PcPu} = 18.8$ Hz.

*2.3. Preparation of [CpRu(PPh_3)(η^2-$Ph_2PN(H)PPh_2$)]Cl (**6**)*

A solution of $Ph_2PN(H)PPh_2$ (0.026 g, 0.068 mmol) in toluene (8 ml) was added dropwise to a solution of $CpRuCl(PPh_3)_2$ (0.050 g, 0.068 mmol), also in toluene (10 ml) and the reaction mixture was heated to reflux for 3 h. A clear solution was obtained. The solution was cooled to r.t. and 3 ml of *n*-hexane was added. An orange/yellow-colored crystalline product was precipitated, which was isolated by filtration and then dried under vacuum.

When the above reaction was carried out in methanol under refluxing conditions the same product **6** was formed.

Orange/red crystals, yield 87% (0.049 g), m.p. 201–203°C. Anal. Found: C 65.78, H 4.81, N 1.51%. Calc. for $C_{47}H_{41}NP_3ClRu$: C 66.47, H 4.83, N 1.65%. IR (KBr) ν_{max}: 3122s, 3055m, 2910m, 2822s, 1198sh, 1170sh, 1048m, 812s, 805sh cm^{-1}. ^1H-NMR ($CDCl_3$): δ Phenyl region, 7.28 (m, 35H), δ Cp, 4.42 (s, 5H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ (P_r) 58.0 (d), δ (PPh_3) 49.1 (t), $^2J_{PP} = 36.6$ Hz.

*2.4. Preparation of [CpRu(PPh_3)(η^2-$Ph_2PN(Ph)PPh_2$)]Cl (**7**)*

A solution of $Ph_2PN(Ph)PPh_2$ (0.032 g, 0.068 mmol) in toluene (8 ml) was added dropwise to a solution of $CpRuCl(PPh_3)_2$ (0.05 g, 0.068 mmol), also in toluene (8 ml) and the reaction mixture was stirred at r.t. for 6 h. During that period a yellow crystalline product was separated from the reaction mixture. The solution was cooled to r.t. and the product was isolated by filtration and dried under vacuum.

The above reaction was carried out in 1:2 and 1:3 molar ratios at 80–100°C in toluene to give the same product in almost quantitative yield.

Light yellow crystals, yield 95% (0.061 g), m.p. 223–225°C. Anal. Found: C 68.98, H 4.91, N 1.42%. Calc. for $C_{53}H_{45}NP_3ClRu$: C 68.83, H 4.87, N 1.51%. IR (KBr) ν_{max}: 3054m, 2927sh, 2853s, 1968w, 1633sh, 1699sh, 1486sh, 1224m, 1090sh, 1020s, 930sh, 889sh cm^{-1}. ^1H-NMR ($CDCl_3$): δ Phenyl region, 7.32 (m,

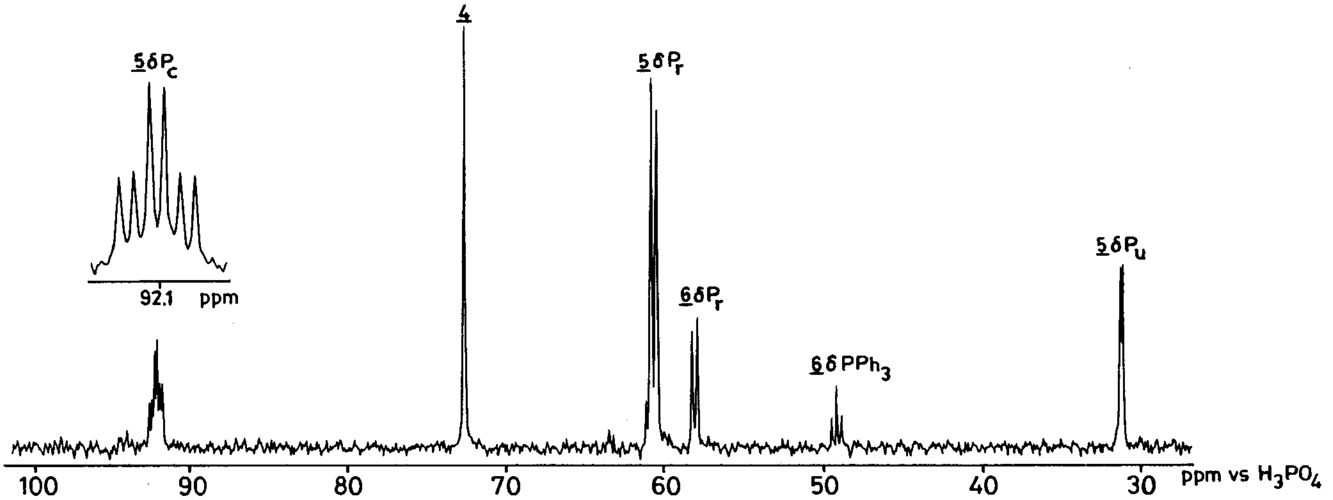


Fig. 1. $^{31}P\{^1H\}$-NMR spectrum of reaction mixture containing compounds **4**, **5** and **6**.

40H), δ Cp, 4.41 (s, 5H); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ (P_r) 79.0 (d), δ (PPh_3) 45.0 (t), $^2J_{PP} = 33.26$ Hz.

2.5. Preparation of [CpRu(PPh$_3$){η^1-(C$_6$H$_4$O$_2$)PN(Ph)P(O$_2$H$_4$C$_6$)}$_2$]Cl (*8*)

A solution of ($C_6H_4O_2$)PN(Ph)P($O_2H_4C_6$) (0.025 g, 0.067 mmol) in toluene (8 ml) was added dropwise to a solution of $CpRuCl(PPh_3)_2$ (0.050 g, 0.068 mmol) in the same solvent (10 ml) and the reaction mixture was heated to 80°C for 6 h. During that period a yellow crystalline product was separated. The solution was cooled to r.t. and the precipitate was isolated by filtration and dried under vacuum.

Pale yellow crystals, yield 56% (0.045 g), m.p. 171–173°C. Anal. Found: C 61.54, H 4.30, N 2.21%. Calc. for $C_{59}H_{46}N_2O_8P_5ClRu \cdot C_6H_5CH_3$: C 61.21, H 4.2, N 2.16%. IR (KBr) ν_{max}: 3066vs, 3029s, 1600s, 1478vs, 1228s, 942sh, 1096w, 1008sh, 824m, 729s, 526m cm^{-1}. ^1H-NMR ($CDCl_3$): δ Phenyl region, 7.32 (m, 41H), δ Cp, 4.40 (s, 5H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ (PPh_3) 53.6 (t), δ (P_c) 169.6 (dd), δ (P_u) 141.7 (d), δ ($P_{u'}$) 140.5 (d), $^2J_{PPc} = 54.4$ Hz, $^2J_{PcPu} = {}^2J_{Pc'Pu'} = 55$ Hz.

The yield of **8** was improved to 85% when the stochiometry of the reactants i.e. the metal to the ligand was increased to 1:2 molar ratio.

2.6. Preparation of [(η^5-Cp$_5$H$_5$)Ru(η^2-Ph$_2$PN(Ph)PPh$_2$)(CO)]Cl (*9*)

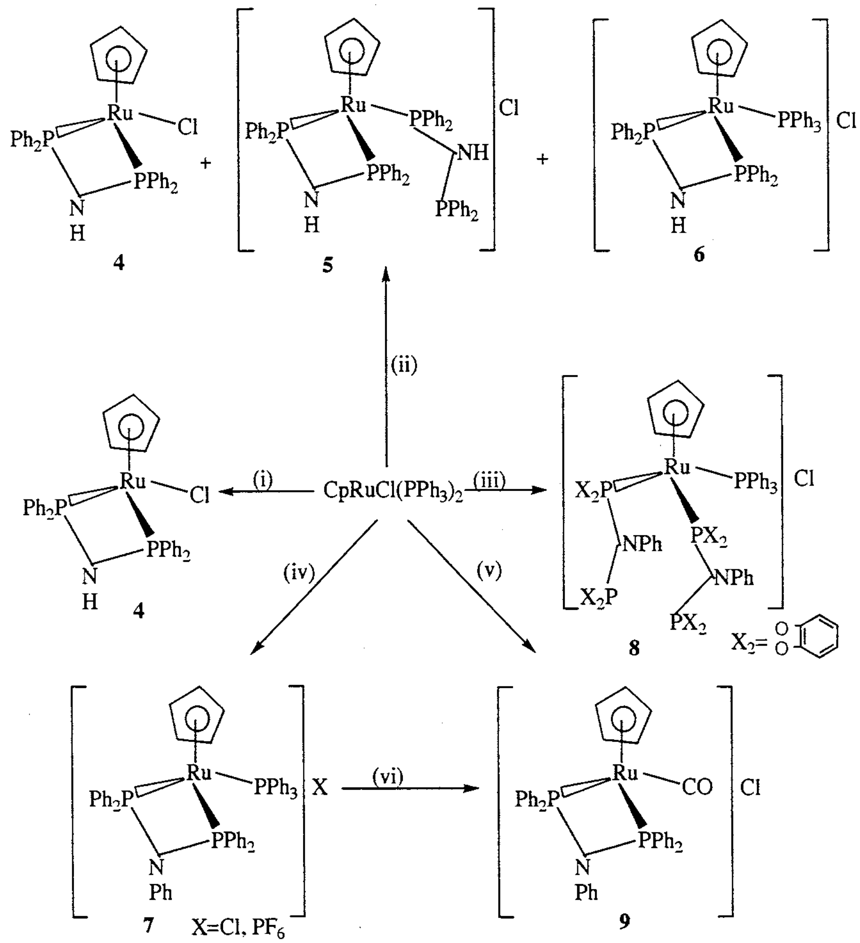
A solution of $Ph_2PN(Ph)PPh_2$ (0.037 g, 0.070 mmol) in toluene (8 ml) was added dropwise to a solution of $CpRuCl(PPh_3)_2$ (0.051 g, 0.070 mmol), also in toluene (8 ml) while CO gas was bubbled through the solution. After the completion of the addition the reaction mixture was heated to 100°C for 4 h. A clear yellow solution was obtained. Solvent was removed under reduced pressure to afford a yellow residue. The residue was extracted with 12 ml of *n*-hexane to remove free PPh_3. The remaining residue was dissolved in 3 ml of dichloromethane and diluted with 1 ml of *n*-hexane and cooled to 0°C to give pale yellow crystals of [(η^5-C_5H_5)Ru(η^2-$Ph_2PN(Ph)PPh_2$)(CO)]Cl (**9**).

Pale yellow crystals, yield 75% (0.041 g), m.p. 218°C (decomposes). Anal. Found: C 62.31, H 4.18, N 1.98%. Calc. for $C_{36}H_{30}NOP_2RuCl$: C 62.56, H 4.34, N 2.02%. IR (nujol) ν(CO): 1957 cm^{-1}; other bands, ν_{max}: 2921s, 2858m, 1641m, 1597m, 1458s, 1375s, 1360sh, 1104m, 930m, 742s, 693s cm^{-1}. ^1H-NMR ($CDCl_3$): δ phenyl region, 7.34 (m, 15H), δ Cp, 4.42 (s, 5H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 48.0 (s).

3. Results and discussion

The reaction between (η^5-C_5H_5)$RuCl(PPh_3)_2$ and bis(phosphino)amines is profoundly affected by the steric and electronic properties of two donor phosphorus atoms as well as the substituents on the bridging nitrogen center.

Reaction of (η^5-C_5H_5)$RuCl(PPh_3)_2$ with $Ph_2PN(H)PPh_2$ (**1**) in toluene solution in a ratio of 1:1 at 70°C for 6 h gives an orange/red solution. The solution was concentrated and cooled to 0°C. The orange/red crystals of the neutral complex **4** formed from this solution were separated and dried in vacuo. The yield was 78%. The ^{31}P-NMR spectrum of compound **4** shows a singlet at 72.6 ppm indicating that both the PPh_3 ligands are replaced by $Ph_2PN(H)PPh_2$ which is acting as a bidenate chelating ligand. The reaction of (η^5-C_5H_5)$RuCl(PPh_3)_2$ with two equivalents of $Ph_2PN(H)PPh_2$ yielded an orange/yellow product. The ^{31}P-NMR spectrum of the product (Fig. 1) indicated that it is a mixture of three products, **4**, **5** and **6**



Scheme 1. Reaction pathway indicating the structures **4**–**9** and the conditions necessary for the reactions to occur.

as shown in Scheme 1. A singlet at 72.6 ppm was assigned to the compound **4**. Compound **6** exhibits a doublet at 58.0 ppm for chelating $Ph_2PN(H)PPh_2$ and a triplet at 49.1 ppm for PPh_3 with a $^2J_{PP}$ value of 36.6 Hz. Compound **5**, with two $Ph_2PN(H)PPh_2$ ligands, shows three sets of ^{31}P-NMR resonances with relative intensities of 1:2:1, which is consistent with this structural formulation. The doublet at 60.6 ppm was assigned to the chelating $Ph_2PN(H)PPh_2$ which is coupled to the metal bound phosphorus of the monodentate ligand with a $^2J_{PP}$ value of 40.4 Hz. The relatively low field shift of coordinated phosphorus atom of the monodentate $Ph_2PN(H)PPh_2$ when compared to that of chelating $Ph_2PN(H)PPh_2$ is a direct consequence of chelate-ring contribution [39]. The resonance due to coordinated phosphorus center appears at 92.1 ppm as a triplet of doublets. The uncoordinated phosphorus center appears at 31.2 ppm as a doublet with a $^2J_{PP}$ value of 18.8 Hz. The compounds **4** and **5** were prepared in their pure form separately using different reaction conditions.

The reaction of $Ph_2PN(Ph)PPh_2$ (**2**) with $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ afforded only the chelated cationic complex **7**, even in the presence of an excess of bis(phosphino)amine ligand under different reaction conditions. The ^{31}P-NMR spectrum of the compound **7** is similar to that of compound **4**. The triplet at 45 ppm is assigned to PPh_3 whereas the resonance due to the chelating ligand appears as a doublet at 79.0 ppm with a two bond P–P coupling of 33.3 Hz. When the above reaction was carried out while CO gas was bubbled through the solution, a carbonylated product **9** was formed in quantitative yield. The IR spectrum of **9** shows a ν(CO) at 1957 cm^{-1} indicating the presence of a carbonyl group on the ruthenium center. Further evidence for the carbonylation and the subsequent elimination of PPh_3 group came from ^{31}P-NMR data. The ^{31}P-NMR spectrum of the complex **9** shows a singlet at 48.0 ppm indicating the presence of only the chelating $Ph_2PN(Ph)PPh_2$. The complex **9** can also be prepared by bubbling the CO gas through a solution of **4** in toluene at 50°C.

The reaction of catechol derivative $(C_6H_4O_2)PN(Ph)P(O_2H_4C_6)$ (**3**) with $(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2$ in equimolar quantities afforded a rather interesting cationic compound **8** containing one triphenylphosphine and two monodentate bis(phosphino)amine ligands. The ^{31}P-NMR spectrum (Fig. 2) is

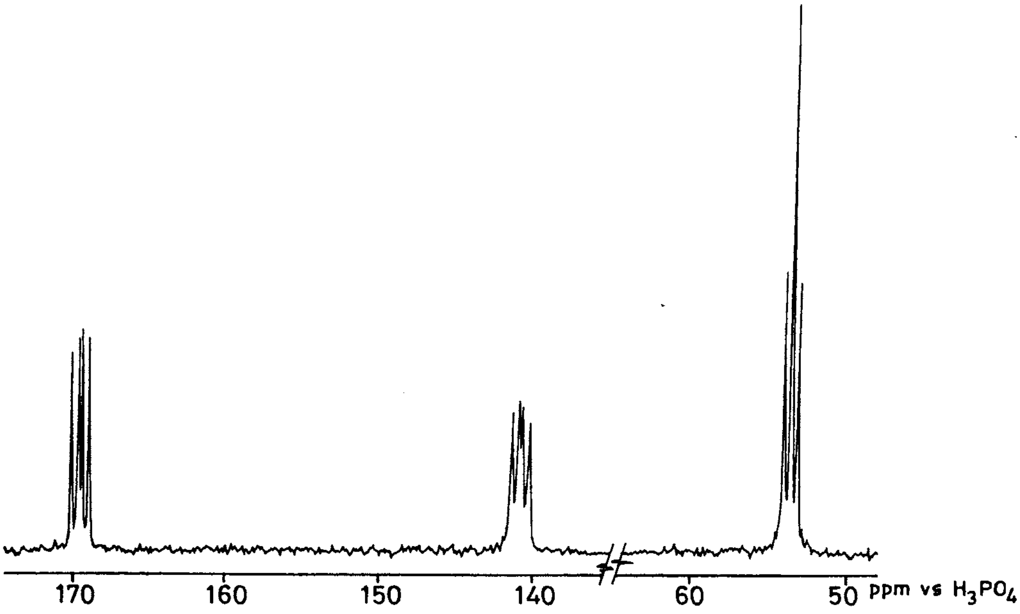


Fig. 2. $^{31}P\{^1H\}$-NMR spectrum of compound **8**.

quite consistent with the structure. The phosphorus resonance due to the triphenylphosphine appears at 53.6 ppm as a triplet. The resonance at δ 69.6 arises from coupling to the triphenylphosphine center and one uncoordinated phosphorus center is assigned to two coordinated phosphorus centers of monodenate ligands. For the catecholato monodentate ligands the two coordinated phosphorus centers are effectively magnetically equivalent (same δ value and coupling to PPh_3) even though the two uncoordinated atoms are inequivalent (differing δ values but identical coupling to the bound P atom), presumably due to folding and conformation effects. The two uncoordinated phosphorus centers appear as two doublets having very similar chemical shift values (δ 141.2 and δ 140.5) close to that of free ligand **3** (δ 130.9). The uncoordinated phosphorus centers do not show any long range coupling with triphenylphosphine.

These observations are similar to those made for the related bis(dimethylphosphino)methane complexes [7]. However, unlike dppm/Ru(II) chemistry [1,2], the product formation in our work is not affected by the polarity of the solvents. For the dppm complexes, the cationic species only resulted when polar solvents were used and neutral complexes were formed when aromatic hydrocarbons were employed.

4. Conclusion

The reactions of various bis(phosphino)amines with $[CpRuCl(PPh_3)_2]$ have led to the formation of different types of mononuclear complexes depending on the substituents on both the phosphorus centers and also on the bridging nitrogen atom. This once again demonstrates the versatility of bis(phosphino)amine ligands. The steric and electronic influence of substituents on phosphorus centers will directly control the donor and acceptor ability of these class of ligands that in turn dictates their coordination modes. Many of these complexes containing monodentate bis(phosphino)amines could act as metalloligands toward transition metal, to form a series of homo- and/or heterobimetallic complexes. Further work in this direction and in possible utilization of these complexes for catalytic purposes is in progress.

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[36] ^{1}H-NMR of compounds **4** and **8** show the resonances due to the co-crystallized toluene which is consistent with the observed microanalysis data.
[37] Key to IR band absorption intensities: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.
[38] Key to NMR peak multiplicities: δ P_r, phosphorus atoms in the chelate ring; δ P_u, uncoordinated phosphorus center; δ P_c, coordinated phosphorus center; s, singlet; d, doublet; t, triplet; td, triplet of doublets.
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